

Raoult's Law and the Equilibrium Vaporization of Hydrocarbon Mixtures

by
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RAOULT'S LAW AND THE EQUILIBRIUM VAPORIZATION OF HYDROCARBON MIXTURES

BY MARVIN C. ROGERS¹ AND GEO. GRANGER BROWN

INTRODUCTION

The vaporization of hydrocarbon mixtures is of fundamental importance to the entire petroleum industry. In addition to this process, the natural gasoline industry is also interested in the reverse process, absorption.

In treating the vaporization of hydrocarbon mixtures it has generally been assumed that Raoult's Law held with sufficient accuracy for engineering calculations at least. But apparently no quantitative study has been reported to show that this assumption has been justified.

Raoult's Law may be stated in ordinary terms as follows: "In an ideal solution of like components, the partial pressures exerted by the components are proportional to their mol fractions in the solution." This means that the partial pressure in the vapor phase should be equal to the product of the mol fraction of a component in the liquid by its vapor pressure in the pure state.

E. H. Leslie and A. J. Good² in "The Vaporization of Petroleum" have studied the relative advantages of both the single flash and successive flash methods of vaporizing hydrocarbon mixtures. While their method of attack and the apparatus used are similar to the ones used in the present investigation, they did not obtain data from which actual comparison with Raoult's Law might be made.

Alex C. Brown and George C. Caine³ in "Studies in Distillation" have gone into the experimental determination of vapor-liquid equilibria in complex hydrocarbon mixtures. Three heavy naphthas from Pennsylvania, California, and Mid-Continent crudes were studied.

¹ This paper forms part of a thesis submitted by Marvin C. Rogers to the Graduate School, University of Michigan, in partial fulfillment of the requirements for the degree, Doctor of Philosophy.

² *Ind. Eng. Chem.*, 19, 453 (1927).

³ *Amer. Inst. Chem. Eng.*, Aug., 1928, meeting. Publications M. I. T., Contribution No. 230 from Dept. of Chem. Eng., 1928.

A single equilibrium vaporization was made on each of the samples and the overhead and bottoms were analyzed in a "true boiling point" column similar to that described by Peters.⁴ From these data and the amounts vaporized in the equilibrium vaporization, a method was developed whereby approximate overall deviations from Raoult's Law could be determined over the range of the compounds contained in the naphthas. The choice of the vaporization temperature or the amount to be vaporized was apparently optional and not predetermined. The results of the investigation indicate that in the naphthas studied, the calculated vaporizations varied as much as 10 to 15 per cent from those which would be indicated by Raoult's Law. Inasmuch as this study was based entirely upon a single vaporization of each of three naphthas there may be some question as to whether the variations noted by them apply through wide ranges of vaporization and composition.

R. S. Piroomov and G. A. Beiswenger⁵ have studied the equilibrium vaporization of oils in a manner similar to that used by Leslie and Good.² Three of these oils were crudes of different characteristics, and three others were lighter stocks obtained from various crudes. Analyses were made in a "true boiling point" column. Theoretical vaporizations were calculated by means of Raoult's Law using vapor pressures obtained from the Cox⁶ chart, and compared with the experimental results. The apparatus used for vaporization was very similar to that used in the present investigation. Agreement between calculated and observed results was good except in the case of small amounts vaporized from mid-continent crude. The results of this investigation seem to indicate that an equilibrium vaporization curve may be calculated by means of Raoult's Law with reasonable accuracy for any of the types of oils studied.

The only work which bears directly upon the present problem of a mixture of natural gasoline hydrocarbons, is that done by W. J. Podbielniak and G. G. Brown.⁷ Two types of vaporization were studied, the differential, and equilibrium flash. Raoult's Law was used as a basis of calculation and curves were given to show the good agreement between the calculated and experimental results.

⁴ *Ind. Eng. Chem.*, 18, 69 (1926).

⁵ A. P. I. Proceedings, 9th annual meeting, Dec., 1928.

⁶ *Ind. Eng. Chem.*, 15, 599 (1923).

⁷ *Proceedings of the Seventh Annual Convention, Natural Gasoline Association of America*, p. 72 (1928).

The differential vaporization was carried out in a vaporized heated by means of a well agitated oil bath and fitted with the necessary stirring mechanism and outlets for liquid and vapor samples. The original sample for the differential vaporization had the following analysis:

	Per cent
Propane	1.4
Iso butane	4.7
Normal butane	22.6
Iso pentane	11.1
Normal pentane	20.3
Iso hexane	8.5
Normal hexane	14.7
Residue	16.7

This analysis is similar to sample 72 studied in the present investigation.

Only one equilibrium flash distillation was made. For this study one of the mixtures considered in the present investigation (sample 48) was used.

For making analyses of the vapor and liquid, Podbielniak⁸ developed a fractionating column very similar to the apparatus used in this investigation.

The results obtained indicate that there is a slight tendency for the lighter components in a mixture to be more volatile and the heavier components to be less volatile than would be calculated by Raoult's Law. This finding was somewhat to be expected from the work of Calingaert and Hitchcock.⁹ The importance of extreme care in the analyses of the mixtures used was not properly appreciated as evident in the poor separation of the isomeric compounds. These inaccuracies in analysis and the fact that only one sample was used in the differential vaporization and only one vaporization in the flash vaporization, limit the following conclusions which were put forth by these authors.

1. The gas-free vapor pressure of the natural gasolines can be determined from the analysis by using Raoult's Law.

2. That in computing partial vapor pressures of the individual components, the lower boiling constituents exert a higher and the higher boiling a lower partial pressure than would be computed by Raoult's law.

⁸ *Refiner and Nat. Gasoline Mfgr.*, 8, 3, 55 (1929); *Oil and Gas Journal*, 27, 35, 38 (Jan. 17, 1929).

⁹ *Jour. Amer. Chem. Soc.*, 49, 750 (1927).

3. The maximum deviation from the computed partial pressure in complex mixtures of paraffin hydrocarbons such as natural gasoline seldom exceeds five per cent of the partial pressure.

4. Vaporization processes can be computed with satisfactory accuracy for natural gasolines by the use of Raoult's law.

During the course of work on the "Equilibrium-Air Distillation of Motor Fuels" conducted by E. M. Skinner and G. G. Brown¹⁰ it was observed that when the equilibrium vaporization curves of several fuels were compared with the curves computed from the analysis, different deviations for different samples were observed. Mixture 48 had a pronounced positive deviation when small amounts were vaporized, and a similar negative deviation from Raoult's law when large amounts were vaporized. This mixture was the same one used in the study of flash vaporization by Podbielniak. It so happened that the vaporization performed by Podbielniak was in the neighborhood of 34 per cent vaporized which is very near to the percentage vaporization that agrees with that calculated by Raoult's law, although pronounced deviations at other amounts vaporized are evident. This peculiar deviation formed the basis for part of the work of the present investigation.

ABSORPTION OILS

Absorption is simply the reverse of vaporization and since it is so important a part of the natural gasoline industry it might well be considered with the study of vaporization. In absorption as well as in vaporization, Raoult's Law has been assumed to be correct, in the absence of any experimental data.

Robert E. Wilson and Edward P. Wylde¹¹ in "Vapor Pressure of Volatile Solvents," have studied the actual vapor pressures exerted by benzene, hexane, and cyclohexane; in California oil, an asphalt-base oil, a paraffin-base oil, and in castor oil. In the case of hexane, which represents the type of compound found in natural gasoline, the agreement with Raoult's law was good when dissolved in the paraffin-base oil and in the asphalt-base oil, but a considerable deviation was observed in the castor oil. This behavior was to be expected because

¹⁰ E. M. Skinner, Dissertation, U. of Michigan, 1929. Presented before Am. Chem. Soc., April 29, 1929.

¹¹ *Ind. Eng. Chem.*, 15, 801 (1923).

of the dissimilarity between the molecules of hexane and of castor oil. In general, the deviations were not striking for any of the compounds studied when in solution in the paraffin-base and the asphalt-base oil.

R. E. Wilson and H. S. Davis¹² studied seven different absorbing oils by measurement of vapor pressures of solutions of benzene in these oils. It was found that the relative absorption efficiencies, i.e., volume of benzene absorbed per unit volume of absorbent at the same temperature and vapor pressure, were about the same for the different oils. Benzene, however, cannot be compared directly to natural gasoline because of its molecular structure.

George Calingaert and Lauren Hitchcock⁹ reported vapor pressure data and deviations from Raoult's Law for the following pairs of compounds: butane-pentane, pentane-heptane, butane-benzene, and butane-straw oil. The values of the deviations given at 20 per cent of the lighter component are: for butane-pentane, 4 per cent; for butane-heptane, 0 per cent; for pentane-heptane, 7 per cent; for butane-benzene, 64 per cent; and for butane-straw oil, —2.6 per cent. No definite conclusions can be drawn from these data as to what might be expected from a ternary or more complex mixture, but in general the deviations seem to be quite erratic.

The natural gasoline industry is obviously interested in the study of absorption oil and is trying to establish specifications that are based upon something more than guesswork. The work already done does not appear to be very conclusive and none of it has established the validity of Raoult's Law.

A. F. Maxson¹³ made a short study of two absorption oils, one of which he termed a long range oil with an initial boiling point of 500 degrees F., and the end point at 700 degrees F. The other oil having an initial boiling point of 442 degrees F. and an end point at 460 degrees F. he called a narrow range oil. Vapor pressure data were taken on samples of oil and gasoline varying in composition from 1 to 20 per cent gasoline by weight. The short range oil showed the lowest vapor pressure and might be termed the better oil for absorption purposes. This is in agreement with Raoult's Law, since the short range oil had a lower molecular weight and the mol fraction of gasoline was somewhat lower for a given weight per cent

¹² *Ind. and Eng. Chem.*, 15, 947 (1923).

¹³ *Proc., Assn. of Nat. Gasoline Mfgs.*, p. 25 (1925).

than it was in the high boiling long range oil. The other considerations which he mentions are mechanical and are principally concerned with the handling of the oil in an absorber.

A. L. Davis ¹⁴ in study of an ideal absorption oil for natural gasoline, calculated by Raoult's Law, vapor pressures for binary mixtures of hydrocarbons, and found that the following combinations gave the lowest total pressure for a given composition:

<i>Solute</i>	<i>Solvent</i>
Ethane	Hexane
Propane	Hexane
Butane	Octane
Pentane	Decane
Hexane	Decane

In his experimental work he mixed a representative gasoline whose composition gave it a molecular weight of about that of pentane, with several compounds and found that the ideal absorbent for the mixture was a compound with molecular weight approximately 28 units higher than decane which he computed to be the best absorbent for a mixture of this composition. L. D. McLouth ¹⁵ made a similar study and came to the same conclusions as Davis.

In Europe a considerable amount of interest has been displayed in the use of Tetralin (Tetrahydronaphthalene) for gas scrubbing and absorption of all sorts of materials from gas. G. Weissenberger ¹⁶ conducted some experiments on the properties of tetralin as a natural gasoline absorbent, and has shown its superiority over spindle oil and gas oil. His work shows a better removal of gasoline from the gas by the tetralin than the other oils. He does not give, however, molecular weight data from which one can compute the relative values of absorption from Raoult's law, and from the values which are given, it seems that Raoult's law holds fairly well, and that the difference in the amount absorbed is due to the low molecular weight of the tetralin. The molecular weights of the spindle oil and the gas oil are certainly higher than that of tetralin which is 134. The data reported are such as would be indicated by Raoult's Law under these conditions.

¹⁴ *Proc., Assn. of Nat. Gasoline Mfgs.*, p. 37 (1926).

¹⁵ *Nat. Pet. News*, 20, No. 32, 54 (1928).

¹⁶ *Petroleum*, 20, 33, 1817-25 (1925).

Experimental Work

EQUILIBRIUM VAPORIZER

The apparatus used to obtain the vapor-liquid equilibria in this investigation was similar to that described by Leslie and Good, and Podbielniak and Brown. Good found that this apparatus gave equilibrium independent of feed-rate over a range of 6 to 15 cc. per minute.

The apparatus shown in Fig. 1 was designed to operate continuously. It consisted of a feeding burette *A* surrounded by the jacket *B* in which was circulated cold brine to prevent vaporization. The burette was made of two iron pipes welded together and fitted for circulation of brine through the annular space between them to prevent vaporization. The feed was regulated by the drops as they fell into the enlargement *D* which was a glass tube.

The feed dropped directly into the heating coil *G*. This coil consisted of about 5 feet of standard $\frac{3}{8}$ -inch pipe bent into a helix of 3 inches diameter.

The heating coil discharged upward into the bottom of the reaction chamber *I*. This chamber consisted of a cylindrical vessel $3\frac{1}{2}$ inches in diameter and 5 inches long, the bottom of which was permanent and the top bolted with a flange. The top carried a thermometer well and a vapor outlet. The liquid drain was in the bottom. The chamber was filled with $\frac{1}{2}$ -inch Lessing rings to provide a large surface. In the center of the chamber was a modified Cottrell pumping tube *K* formed from a piece of $\frac{3}{4}$ -inch pipe and a standard cap, to which was brazed three pieces of $\frac{1}{4}$ -inch outside diameter seamless steel tubing, each with a slight curvature. The liquid and vapor from *G* were discharged under the pumping tube. The vapor in separating from the liquid rose through the tubes giving the effect of a 'jet-lift.' This kept the packing wet with the liquid, greatly increasing the time of contact. The vapor passed to the condenser *L*. The liquid drained to the bottom of the chamber and flowed out through the cooler *N*. The liquid was kept in constant circulation by the action of the pumping tube. The depth of the liquid was controlled by raising or lowering the adjustable pipe *O*.

The constant temperature bath *H* was constructed of steel heavily insulated. The liquid level was kept high enough to cover completely the equilibrium chamber and the outlet. Under these condi

tions no condensation could occur in the vapor tube. The heating medium was an oil heavy enough to prevent vaporization at the temperatures used. Heat was supplied by the electric heating element *U*.

The vapor temperature was indicated by thermometer *Y* placed

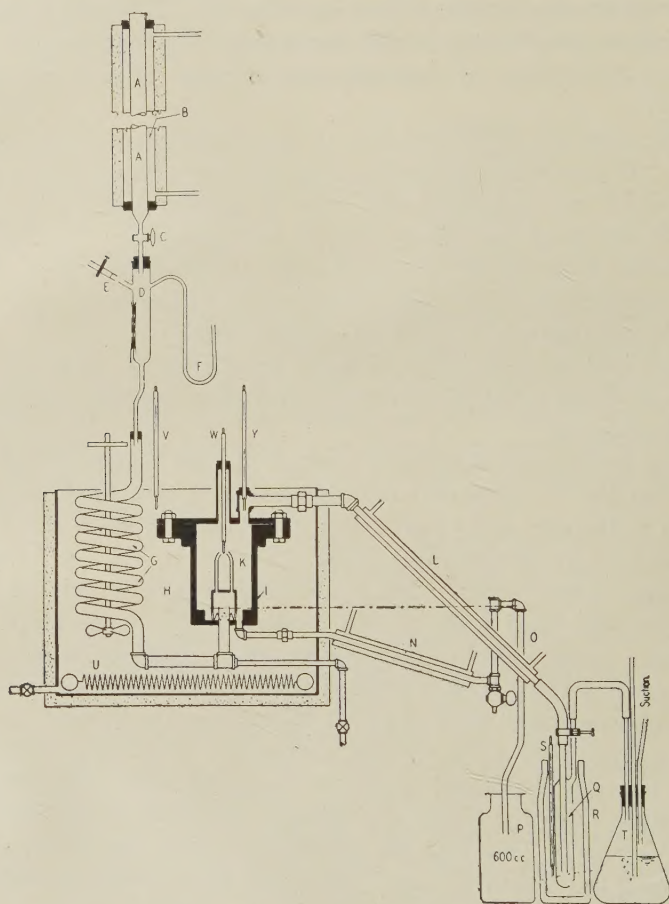


FIG. 1. Equilibrium Vaporization Apparatus.

in the vapor outlet. Thermometer *W* gave the liquid temperature, while thermometer *V* gave the bath temperature. Thermometer *W* was dispensed with during the latter part of the investigation because of the close agreement between it and the vapor temperature thermometer. The condenser *L* and the cooler *N* were of double pipe

construction with brine circulation through the annular space. Further condensation of the vapors was obtained in the glass trap *Q* which was immersed in a vacuum bottle *R*, full of natural gasoline and carbon dioxide snow at a temperature of -79°C . The upper

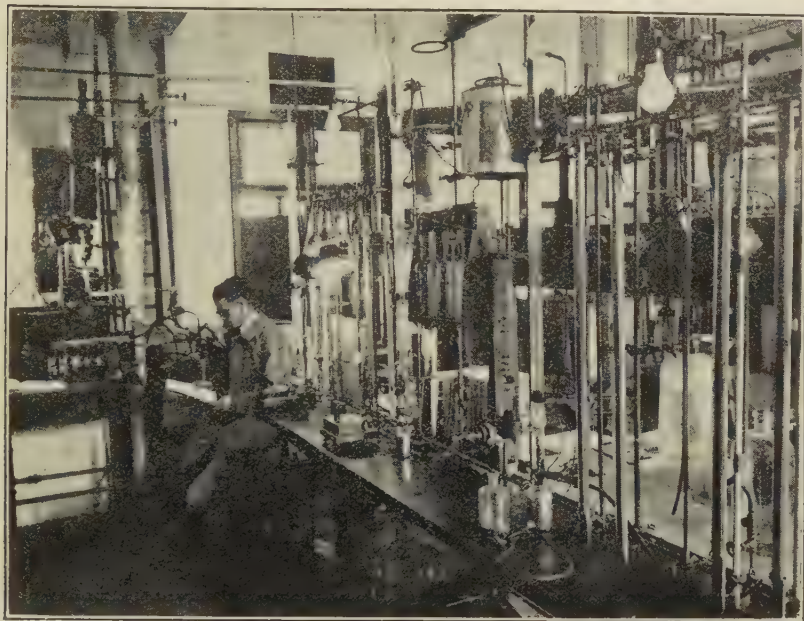


FIG. 2. Equilibrium Vaporizer and Low Temperature Fractionation Apparatus.

part of the connection to the glass trap led to a manometer filled with oil. During the runs this manometer was kept at zero and the pressure regulated by the regulating device *T*. A bimetal temperature regulator connected through a relay to the heating element was used to control the temperature of the bath.

EXPERIMENTAL PROCEDURE

Previous to a run, the bath was heated to the desired temperature and the thermostat adjusted. The sample to be vaporized was placed in the feed burette and kept cool by circulating cold brine through the jacket. The liquid remaining in the apparatus from the previous runs was drained and the sample allowed to run into the vaporizer from the burette. When the liquid bottoms from the vaporizer be-

gan to run out from the outlet *O* the burette was drained and a weighed sample placed in it. The trap *Q* was attached to the outlet of the overhead vapor condenser, and the bottoms receiver *P* placed under the outlet for the bottoms *O*. Both of these receivers were weighed empty.

With the receivers in place the sample was fed into the vaporizer and the feed governed so as not to exceed 10 cc. per minute, as this rate was known to be below the maximum at which equilibrium is obtained. This had been determined by Leslie and Good² for the same type of apparatus, by vaporizing a chloroform-toluene mixture and checking the analysis of the liquid bottoms against the analysis of the overhead vapor.

The feed was allowed to run until sufficient overhead and bottoms were obtained for analysis. Then the remaining sample in the burette was drained back into the sample can to determine the actual amount used. The liquid bottoms and the overhead vapor condensate were then weighed to determine the material balance, and the per cent vaporized.

ANALYTICAL COLUMNS FOR ANALYSES

For any quantitative study of the deviations from Raoult's Law in vapor-liquid equilibria, it is necessary to know the amount of each component present in the original liquid with reasonable accuracy. In the case of binary mixtures this offers no particular difficulty. In studying mixtures of hydrocarbons such as are found in petroleum and natural gasoline, the analysis of liquid mixtures is one of the greatest difficulties encountered.

The apparatus used in this investigation was similar to that described by Podbielniak⁸ and consisted essentially of a fractionating column connected through suitable tubing to an evacuated receiver in which the products of the distillation were collected as a gas. The column was constructed of Pyrex glass and consisted of a tube $3\frac{1}{2}$ to 4 mm. inside diameter and 70 cm. in length. To one end of the column (Fig. 3) the still *B* was attached and to the other end the outlet tube *D* and the reflux chamber *C* were attached. The entire column and reflux chamber, as well as part of the still, were surrounded by a vacuum jacket to prevent radiation and make the column as adiabatic as possible. It was packed with a chromel or copper wire helix coiled so as to fit closely to the side, and cause a maximum surface film of liquid for contact with the rising vapor.

Heating of the liquid in the still was provided by a heating element of No. 30 chromel wire welded to tungsten leads sealed into the glass, providing outside contacts.

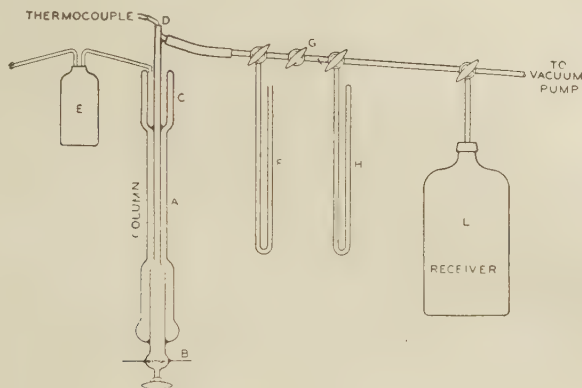


FIG. 3. Low Temperature Fractionation Apparatus.

The cooling of the top of the column was accomplished by syphoning liquid air into a brass container placed in a bath of petroleum ether in the reflux chamber. The temperatures at the top of the column were determined by three copper-constantan thermocouples in series, connected to a millivoltmeter. *F* was an open arm manometer and *H* a closed arm manometer. The products of the distillation were collected in the evacuated receiver *L*.

EXPERIMENTAL PROCEDURE IN FRACTIONATING SAMPLES

In order to prevent changes in composition of the mixtures under investigation the samples were kept in sealed cans or drums and cooled in a brine tank maintained at -20°C . The samples fed to the fractionating column were transferred from the brine-cooled containers to the glass container *Q*, (Figure 1) kept cold in a bath of carbon dioxide snow and ether.

Preliminary to an analysis, the column and the receiver were evacuated to about 1 to 2 mm. with a two stage mechanical vacuum-pump. The top of the column was then cooled to a temperature below that at which the lowest boiling component boils. The sample was then withdrawn from the cooled container and admitted to the still. The pressure on the column, as shown on manometer *F*, was

allowed to come to 760 millimeters and the distillation started. The product from the distillation was removed from the top of the column by cracking the cock *G* and permitting the gas to be drawn into the receiver. The closed arm manometer *H* measured the pressure on the receiver.

During the removal of any one compound the temperature at the top of the column remained practically constant, but when the compound was practically removed from the sample the rate of distillation was decreased and the amount of reflux increased slightly, to obtain close fractionation.

Inasmuch as the compounds were collected as gases, it was essential that the reflux temperature be below that of the room. When the reflux temperature rose to about that of the room, the pressure on the column was reduced. In making the analyses, the compounds through butane were distilled at 760 mm., pentanes at 400 mm., hexanes at 100 mm., and heptanes at 30 mm.

CALIBRATION OF COLUMN AND RECEIVER

It was necessary to know accurately the volume of the receiving bottle *L* in order to determine the amounts of the compounds collected. Although the volume of the receiver had been carefully determined at atmospheric pressure, it was observed during the course of the analyses that the recovery, calculated from the distillate and residue, if any, did not equal the amount of sample originally fed to the column as weighed in the cold glass container *Q*. In all cases the calculated recovery was less than the amount of sample fed, and the loss was greater in the case of samples containing large amounts of hexane and heptane. This led to an investigation of the properties of the hydrocarbon gases when collected in glass containers which have been previously evacuated.

The samples used for the determination of the corrections were, normal heptane, hexanes, pentanes, and isobutane. The normal heptane was obtained from fractionation and was that part of the sample boiling under 760 millimeters pressure at 98.4° C. plus or minus 0.2° C. The hexanes were a mixture of diisopropyl, and normal hexane with less than one per cent of pentane and nothing heavier than hexane in the sample. The pentanes were a mixture of iso- and normal pentane and contained less than 1½ per cent of butane and nothing heavier than pentane. The butane contained over 95 per

cent iso-butane with the remainder normal butane. No attempt was made to prepare the pure compounds because the correction difference between iso- and normal pentane could not be detected in the apparatus used.

Each of these samples was weighed and vaporized in the fractionating column. The change in pressure in the receiver and the receiver temperature were recorded. From these data the amount of the compound actually vaporized could be compared with that calculated using the molal volume of hydrocarbons as 22410 cc. The data so obtained are given in Table I, and the correction factors plotted as a function of pressure at 25° C. in Fig. 4.

TABLE I
DETERMINATION OF CORRECTIONS FOR DISTILLATION ANALYSIS

Compound	Weight of Sample	Receiver Pressure	Room Temp.	Receiver Volume	Grams Recovered	Correction Factor
Butane.....	29.7	488.5	25	19,875	29.4	1.01
Butane.....	6.26	90.0	25	19,875	6.23	1.005
Pentane.....	18.78	238.0	24	19,875	18.41	1.02
Pentane.....	5.46	70.0	24	19,875	5.40	1.01
Pentane.....	29.29	369.0	24	19,875	28.52	1.03
Pentane.....	39.60	495.0	24	19,875	38.01	1.042
Hexane.....	9.90	104.0	25	19,875	9.57	1.036
Hexane.....	11.87	126.3	24	19,875	11.37	1.042
Hexane.....	2.53	30.6	24	19,875	2.48	1.021
Hexane.....	2.64	28.0	24	19,875	2.59	1.020
Heptane.....	2.495	21.7	25	19,875	2.31	1.08
Heptane.....	2.575	21.9	25	19,875	2.33	1.10
Heptane.....	Average correction is 1.09					

One complete set of calculations is given to show the method of determining the correction factors.

Butane—Molecular weight = 58.08
Weight of sample = 29.7 grams
Receiver pressure at start (manometer readings)
Left, 479.7 Right, 497.0
Receiver pressure after vaporization 234.5 723.5
Differences 245.2 226.0
Total pressure change in receiver = 471.2 mm.
Total pressure on receiver = 488.2 mm.
Receiver volume = 19,875 cc.
Receiver temperature = 25° C.
Theoretical amount of butane vaporized.

$$\frac{19875 \times 471.2 \times 58.08}{760 \times 298 \times 22410} = 29.40 \text{ grams.}$$

19875	receiver volume.
471.2	pressure change in receiver.
273	0° C., temperature.
58.08	Molecular weight of butane.
760	One atmosphere in mm.
298	Temperature of determination.
22410	Molal volume of gas.

$$\frac{29.7}{29.4} = 1.01 \text{ or factor for butane at 488.5 mm. pressure.}$$

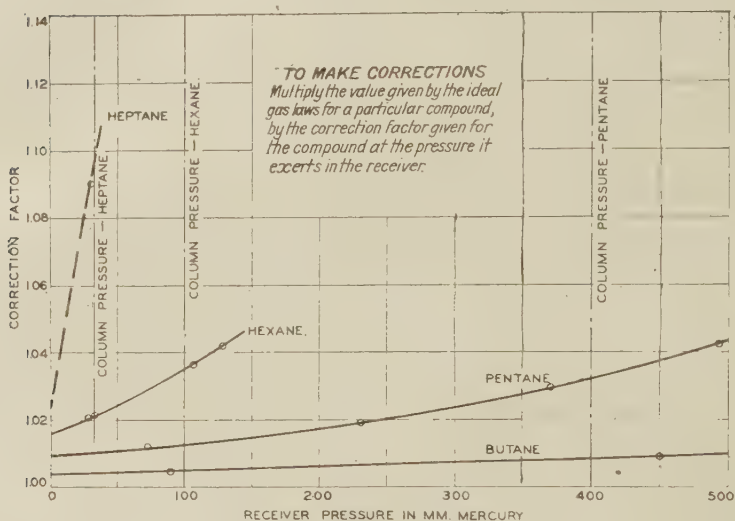


FIG. 4.

The corrections shown in Fig. 4 have been applied to all of the analyses made during this investigation, and the agreement between the recovery and the sample fed has been within one per cent in all cases.

There is an indication from the curves in Fig. 4 that even at zero pressure a correction must be made. This would seem unreasonable from any ordinary considerations because at zero pressure the gases would be expected to act like perfect gases. However, a large part of this correction at practically zero pressure is probably due to changes in the volume of the receiver. The receiver was calibrated at one atmosphere pressure on the outside and on the inside. At low pressures it is probable that the volume of the receiver may be smaller because of the pressure exerted by the atmosphere. However, it is seldom that the amount of compound distilled is low enough to give a pressure less than 10 mm., and, even if due to ex-

perimental error, these corrections at extremely low pressures will introduce no noticeable error in the analysis.

DETERMINATION OF MOLECULAR WEIGHTS

In any experimental work involving the use of Raoult's Law, it is necessary that molecular weights of the various compounds be known. In making the fractional distillation analyses, the boiling points of the compounds give the information desired. However, in practically all of the analyses of heavier liquids there is a residue whose composition is not known. This residue contains a mixture of compounds of unknown composition. In this investigation it was decided that for all practical purposes, an average molecular weight of the residue would serve all purposes. Wilson and Wylde¹⁰ used the freezing-point depression method for determining the average molecular weights of absorption oils. In order to eliminate the possible errors caused by association, they made a series of determinations using various concentrations of oil in benzene. To obtain the molecular weight as at zero concentration in the benzene they plotted the molecular weight as a function of the depression in freezing-point and extrapolated to zero depression which corresponds to zero concentration. Inasmuch as the oils used in this work were obtained from petroleum they contained a mixture of a large number of compounds and any determination made would yield only an average value. The actual procedure which was followed in making the molecular weight determinations was the one which is given by Findlay.¹⁷

Table II gives the data and results for the molecular weight determinations which were made.

TABLE II
MOLECULAR WEIGHT DETERMINATIONS

Sample	Weight of Solute w	Weight of Solvent W	Depression of Freezing Point d	Molecular Wt.
Naphtha.....	.7098	22	.895	184.6
Naphtha.....	.4898	22	.628	180.5
Naphtha.....	.2943	22	.386	177.5

¹⁷ Practical Physical Chemistry, Chapter VII, pages 112-20.

Average Molecular Weight (zero concentration), 172.5

Oil No. 1.....	.1826	22	.203	209.0
Oil No. 1.....	.4405	22	.464	221.0
Oil No. 1.....	.7144	22	.735	226.0

Average Molecular Weight (zero concentration), 204

Residue from Sample 48....	.1939	22	.370	121.7
Res. No. 48.....	.3790	22	.705	125.0
Res. No. 48.....	.5955	22	1.073	129.0

Average Molecular Weight (zero concentration), 118.1

Res. No. 75A.....	.1685	22	.311	125.4
Res. No. 75A.....	.4202	22	.775	126.2
Res. No. 75A.....	.6527	22	1.176	129.1

Average Molecular Weight (zero concentration), 124.3

MATERIALS USED

In this investigation the following mixtures were studied:

1. A natural gasoline, designated as No. 72. The composition of this mixture was obtained by averaging the analyses of the original sample with the sums of the overhead vapors and corresponding residues from the vaporization tests as given in Table V. This method of arriving at the composition was used in order to reduce the errors in a single analysis. In most cases the differences in the analyses are within the experimental error of the analytical method used. Fig. 5 gives the distillation curve of mixture 72.

2. A similar mixture designated as No. 75A. Analytical results and the distillation curve of this mixture are given in Fig. 6.

3. A similar mixture containing the same compounds as 75A, but relatively less pentane, and identified as No. 48. Analytical data are shown in Fig. 7.

4. A synthetic mixture (48A) made by adding to sample No. 48 a sufficient amount of pentane to give a mixture with approximately the same percentage of pentanes as were found in sample 75A, as given below. The pentane sample which was used to prepare 48A had the following composition:

Butane	2.82 Mol. %
Iso pentane	31.20
N-pentane	66.10

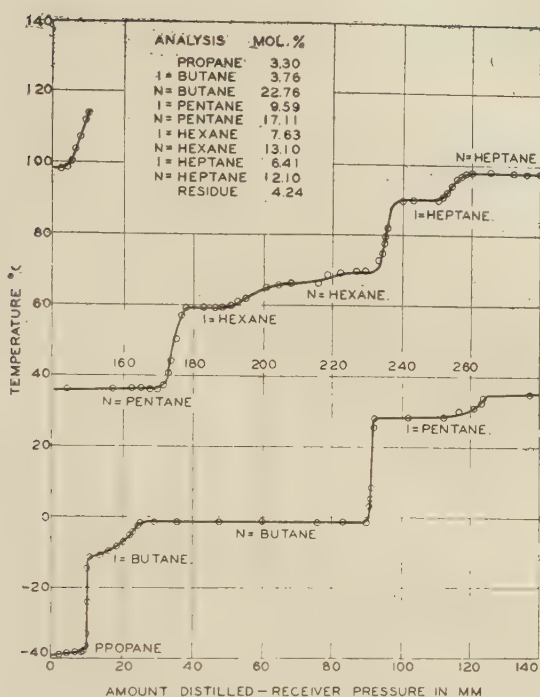


FIG. 5. Fractional Distillation Fuel 72.

PREPARATION OF SAMPLE 48A

Compound	Mols. in 491 gms. of No. 48	Mols. in 32.5 gms. Pentanes	Total Mols.	Analysis of 48A
Butane.....	.242	.012	.254	4.14 Mol %
Iso pentane.....	.706	.133	.839	13.66
Normal pentane.....	1.568	.281	1.849	30.03
Iso hexane.....	.680		.680	11.09
Normal hexane.....	1.000		1.000	16.31
Iso heptane.....	.224		.224	3.66
Normal heptane.....	.423		.423	6.91
Residue.....	.872		.872	14.21

5. A mixture of natural gasoline (89.3 Mol. %) and mid-continent absorption oil (10.7 Mol. %). The oil is designated as No. 1 and its properties (stripped) are given in Table III. This oil was received as a rich oil from the field with the composition as given below :

Compound	Mol. Per Cent
Ethane	.103
Propane	1.537
Iso butane	1.56
Normal butane	4.18
Iso pentane	2.63
Normal pentane	2.28
Iso hexane	.78
Normal hexane	1.20
Iso heptane	.41
Normal heptane	.61
Residue	.88
Absorption oil	83.82

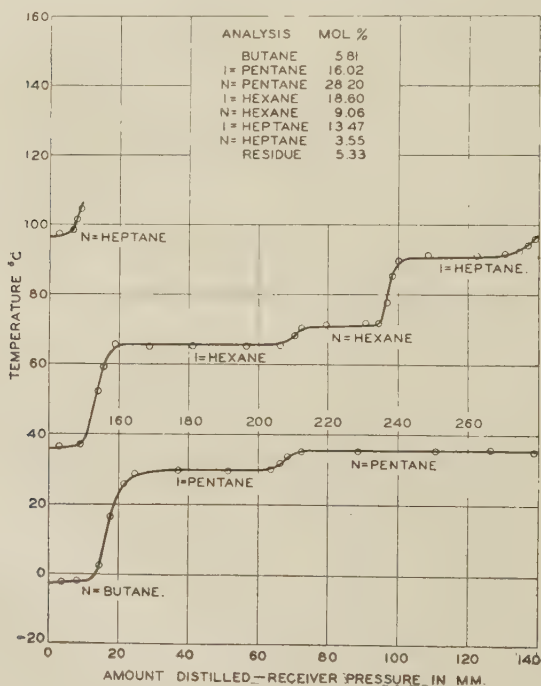


FIG. 6. Fractional Distillation Fuel 75-A.

6. A similar mixture of absorption oil No. 1 containing 73.1 mol per cent of gasoline and having the composition given in Table XIV.

7. A similar mixture of absorption oil No. 1 containing 36.3 mol per cent of gasoline, and having the composition given in Table XVI.

8. A mixture of a naphtha and natural gasoline containing 50 mol per cent of gasoline. The characteristics of the naphtha are given in Table IV.

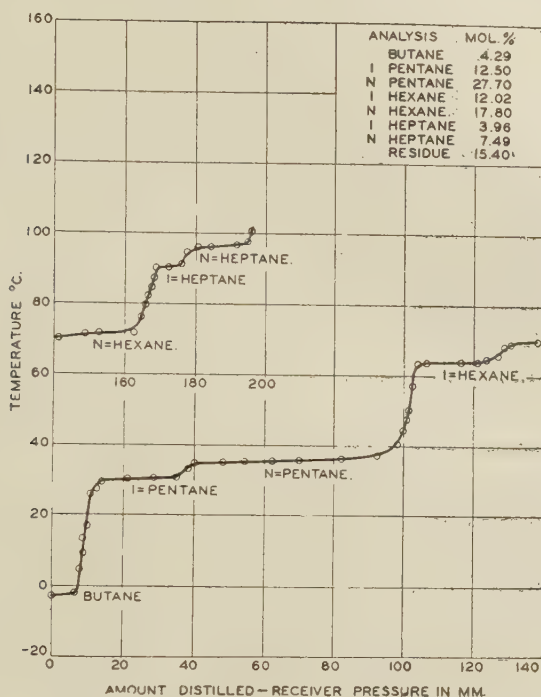


FIG. 7. Fractional Distillation Fuel 48.

TABLE III

PROPERTIES OF ABSORPTION OIL NO. I

Molecular Weight 204	
Specific Gravity 60/60, .8490	
A. S. T. M. Distillation Data	
Initial Boiling Point.....	450 F.
5%.....	491
10%.....	495
20%.....	518
30%.....	531
40%.....	543
50%.....	552
60%.....	572
70%.....	594
80%.....	627
90%.....	680
95%.....	714
End Point above 760 F.	
Recovery 98.5 cc.	

TABLE IV

PROPERTIES OF NAPHTHA SAMPLE

Molecular Weight, 172.3	
Specific Gravity 60/60, .7968	
A. S. T. M. Distillation Data	
Initial Boiling Point.....	285 F.
5%.....	336
10%.....	364
20%.....	394
30%.....	415
40%.....	435
50%.....	444
60%.....	467
70%.....	480
80%.....	496
90%.....	518
95%.....	544
End point 98%.....	562
Recovery 99 cc.	

9. A mixture of tetralin (tetrahydronaphthalene) prepared by the Eastman Kodak Company, and natural gasoline No. 72, containing 50 mol per cent of gasoline.

Results

EXPERIMENTAL

Vaporizations were made on each of the samples at various temperatures with results as given Tables VI, VIII, and shown as dash lines in Figs. 8 through 17.

Data for the vaporization of the individual hydrocarbons in sample No. 72 are given in Table V. The data taken in vaporization tests on the absorption oils enriched by the addition of this same natural gasoline, indicate the same vaporization characteristics as possessed by the natural gasoline itself. Data on the vaporization of the individual hydrocarbons of the enriched absorption oil are not given because the integral vaporization curves (Figs. 8, 12, 13, and 14) supply all of the necessary information.

The following procedure indicates how the weight vaporized as determined experimentally is converted to mol per cent vaporized when the composition of the overhead vapor and either the residue or original are known.

RUN I

731.5 grams fed to the vaporizer, of fuel No. 72.

Molecular weight of No. 72 is 78.73.

$$\frac{731.5}{78.73} = 9.29 \text{ mols of gasoline fed.}$$

84.0 grams were vaporized and analyzed.

46.0 grams of this overhead were analyzed in the analytical column to give 0.7443 mols.

$$\frac{84 \times 0.7443}{46} = 1.36 \text{ mols vaporized.}$$

$$\frac{1.36 \times 100}{9.29} = 14.64 \text{ mol per cent vaporized.}$$

$$\frac{84}{731.5} = 11.50 \text{ weight per cent vaporized.}$$

TABLE V
SUMMARY OF THREE RUNS ON MIXTURE No. 72

Run No.	1			2			3			Average Mol % Analysis Fuel 72	
	Mols Percent in No. 72	Mols in OH	Mols in Bottoms	Total	Mols in OH	Mols in Bottoms	Total	Mols in OH	Mols in Bottoms		Total
Propane	3.22	2.18	1.25	3.43	2.65	.40	3.05	3.44	.12	3.56	3.31
I-Butane	3.56	1.51	1.58	3.09	3.19	.92	4.11	3.81	.30	4.11	3.76
N-Butane	22.10	6.82	17.13	23.95	15.14	6.87	22.01	20.58	3.34	23.92	22.76
Butanes	25.66	8.33	18.71	27.04	18.34	7.79	26.13	24.49	2.64	27.04	26.52
I-Pentane	9.70	1.54	7.17	8.71	4.00	5.61	9.61	6.75	2.70	9.40	9.59
N-Pentane	17.00	1.67	15.88	17.55	6.98	10.90	17.88	12.73	4.27	17.00	17.11
Pentanes	26.70	3.20	23.05	26.25	10.98	16.51	27.49	19.52	6.97	26.49	26.70
I-Hexane	7.66	.38	6.17	6.55	1.38	7.16	8.54	4.26	4.17	8.43	7.63
N-Hexane	12.50	.56	13.86	14.42	1.97	11.16	13.13	6.38	5.99	12.37	13.10
Hexanes	19.56	.94	20.03	20.97	3.35	18.31	21.67	10.63	10.60	20.80	20.73
I-Heptane	6.41										6.41
N-Heptane	12.10										12.10
Residue	6.35		22.30	22.30	.79	20.88	21.67	4.88	18.24	23.12	4.24

$\frac{14.64}{0.7443} = 19.67$ or the factor by which the mols in the sam-

ple for overhead analysis must be multiplied in order to put the analysis on a basis of 100 mols feed. Results of these calculations for entire vaporization of mixture 72 are given in Table V.

TABLE VI

EXPERIMENTAL VAPORIZATION DATA ON NATURAL GASOLINES

Vaporization of No. 72

Run	Vaporization Temperature		Feed (Grams)	Overhead (Grams)	Bottoms (Grams)	Weight % Vaporized
	° C.	° F.				
1	26.7	80	731.5	84.0	640.0	11.5
2	38.9	102	318.4	100.8	216.8	31.5
3	51.2	124	295.0	164.2	130.0	55.7
4	52.3	126.2	159.0	93.0	64.0	58.4
5	62.5	144.5	191.0	148.0	42.5	77.5

Vaporization of No. 75A

6	46.2	115	392	70.2	321.0	17.9
7	51.7	125	223.5	89.5	133.0	40.1
8	60.5	141	137.0	90.5	46.5	66.0
9	67.2	153	195.0	157.7	37.0	80.8

Vaporization of No. 48

(Data from Skinner marked S and from Podbielniak, P)

10	41.2	106	536.1	2.0	533.0	.4
11	74.0	165	135.6	112.6	23.5	83.0
12	63.0	145	135.6	81.4	64.0	60.0
13	52.2	126	422.0	121.0	302.5	28.6
14	46.0	115	169.5	29.7	140.0	17.5

Vaporization of No. 48A

15	50.5	123	249.0	41.0	207.0	16.5
16	77.7	172	104.0	87.0	18.0	83.7

TABLE VII

EXPERIMENTAL VAPORIZATION DATA ON ENRICHED OILS

Vaporization of No. 5

Run	Vaporization Temperature		Feed (Grams)	Overhead (Grams)	Bottoms (Grams)	Weight % Vaporized
	° C.	° F.				
17	93.4	200	344	212.6	132	61.8
18	63.3	146	332	147.0	184	44.3
19	37.8	100	582	101.0	480	17.4
20	54.2	129.5	358	132.5	224	37.0

Vaporization of No. 6

21	93.4	200	545	187	357	34.3
22	62.3	144	547	129.5	417.5	23.6
23	41.7	107	589.5	61.3	525.0	10.3

Vaporization of No. 7

24	62.3	144	1782.0	70.8	1690.0	3.98
25	96.1	205	655.5	45.5	607.0	6.94
26	132.0	270	656.0	84.4	570.0	12.85

TABLE VIII

EXPERIMENTAL VAPORIZATION OF NAPHTHA-GASOLINE MIXTURE NO. 8

Run	Vaporization Temperature		Feed (Grams)	Overhead (Grams)	Bottoms (Grams)	Weight % Vaporized
	° C.	° F.				
27	46.2	115	406	14.5	391.0	3.56
28	65.6	150	373.5	40.0	334.0	10.71
29	77.7	172	245.0	40.0	204.5	16.30
30	90.0	194	295.0	64.5	225.0	21.80

EXPERIMENTAL VAPORIZATION OF TETRALIN-GASOLINE MIXTURE NO. 9

31	63.3	146	493	68.1	425.1	13.8
32	95.3	203.5	356.5	87.5	266.0	24.6
33	77.7	172	230.0	46.5	183.0	20.2
34	50.5	123	341.0	21.5		6.3

CALCULATION OF VAPORIZATION CURVES BY RAOULT'S LAW

In work with complex mixtures the only method which can be used to compute vaporization by Raoult's Law requires a series of trials before the correct value for the vaporization can be obtained. Other investigators¹⁸ have used the trial method for this type of work and have found it quite easy of manipulation. The process consists of equating the partial pressures of the individual components in the vapor phase to the corresponding partial vapor pressures in the liquid phase. In the actual calculations the total pressure and mols vaporized were assumed, and the correct temperature obtained by trial. The following nomenclature was used:

V = Total mols. vaporized on basis of 100 mols feed.

$V_{(\text{with subscript})}$ = the number of vaporized mols of the component indicated by the subscript.

P = Total vaporization pressure, usually 740 mm.

$P_{(\text{with subscript})}$ = Vapor Pressure of the pure component indicated by the subscript at the vaporization temperature.

In the following equations which represent those for calculating the vaporization of mixture 72, the left side is the product of the vapor pressure of the hydrocarbon and its mol. fraction in the liquid. The right side is the product of the vaporization pressure by the mol per cent of the hydrocarbon in the vapor. The figures 3.31, 3.76, 22.76, etc., are the mols of propane, iso-butane, etc., in the original sample.

$$\text{Propane} \left(\frac{3.31 - V_{\text{propane}}}{100 - V} \right) (P_{\text{propane}}) = \frac{V_{\text{propane}}}{V} (740)$$

$$\text{I-Butane} \left(\frac{3.76 - V_{i\text{-butane}}}{100 - V} \right) (P_{i\text{-butane}}) = \frac{V_{i\text{-butane}}}{V} (740)$$

$$\text{N-Butane} \left(\frac{22.76 - V_{n\text{-butane}}}{100 - V} \right) (P_{n\text{-butane}}) = \frac{V_{n\text{-butane}}}{V} (740)$$

$$\text{I-Pentane} \left(\frac{9.59 - V_{i\text{-pentane}}}{100 - V} \right) (P_{i\text{-pentane}}) = \frac{V_{i\text{-pentane}}}{V} (740)$$

¹⁸ Podbielniak and Brown, *Proc., Nat. Gasoline Assn. of America*, 1928. Skinner, Doctor's Dissertation, 1929, U. of Mich.

$$\text{N-Pentane} \left(\frac{17.11 - V_{n\text{-pentane}}}{100 - V} \right) (P_{n\text{-pentane}}) = \frac{V_{n\text{-pentane}}}{V} (740)$$

$$\text{I-Hexane} \left(\frac{7.63 - V_{i\text{-hexane}}}{100 - V} \right) (P_{i\text{-hexane}}) = \frac{V_{i\text{-hexane}}}{V} (740)$$

$$\text{N-Hexane} \left(\frac{13.10 - V_{n\text{-hexane}}}{100 - V} \right) (P_{n\text{-hexane}}) = \frac{V_{n\text{-hexane}}}{V} (740)$$

$$\text{I-Heptane} \left(\frac{6.41 - V_{i\text{-heptane}}}{100 - V} \right) (P_{i\text{-heptane}}) = \frac{V_{i\text{-heptane}}}{V} (740)$$

$$\text{N-Heptane} \left(\frac{12.10 - V_{n\text{-heptane}}}{100 - V} \right) (P_{n\text{-heptane}}) = \frac{V_{n\text{-heptane}}}{V} (740)$$

$$\text{Residue} \left(\frac{4.24 - V_{\text{residue}}}{100 - V} \right) (P_{\text{residue}}) = \frac{V_{\text{residue}}}{V} (740)$$

These equations must be solved for $V_{(\text{subscript})}$ and the individual vaporizations added up to check the total assumed vaporization as shown in Tables IX and X. Usually three trials are sufficient to determine the correct temperature for any given vaporization.

TABLE IX

CALCULATION OF VAPORIZATION OF NO. 72, 30 MOL. % VAPORIZED TEMPERATURE 33.3° C.

Compound	M.W.	Mol. % in Sample	Grams per 100 mols Feed	Mol. % in vapor	Grams per 100 Mols Feed
Propane	44.08	3.31	146.0	2.76	121.5
Iso butane	58.08	3.76	218.0	2.49	145.0
Normal butane	58.08	22.76	1320.0	13.10	761.0
Iso pentane	72.10	9.59	691.0	3.29	237.0
Normal pentane	72.10	17.11	1232.0	4.84	349.0
Iso hexane	86.11	7.63	657.0	1.19	102.3
Normal hexane	86.11	13.10	1128.0	1.41	121.0
Iso heptane	100.13	6.41	642.0	.34	34.0
Normal heptane	100.13	12.10	1212.0	.46	46.0
Residue	118.0	4.24	501.0	.02	2.3
Total		100.00	7747.0	29.90	1914.0

$$\frac{1914 \times 30}{29.9 \times 7747} = 24.8\% \text{ by weight vaporized.}$$

Tables X, XI, XIII, XV, XVII, XVIII give the calculated values for the vaporizations of all of the mixtures studied. The calculated vaporizations of each of the compounds in the mixture is given in the case of the vaporization of mixture 72 and mixtures of 72 and absorption of oil No. 1. In the cases of the other mixtures studied, only the total vaporization is given and compared with the total experimental vaporization as such comparisons are adequate to indicate the deviations from Raoult's Law.

TABLE X
CALCULATED VAPORIZATION OF NO. 72

Compound	10 Mol % Vaporized	50 Mol % Vaporized	70 Mol % Vaporized	90 Mol % Vaporized
Propane.....	1.68	3.12	3.24	3.30
Iso butane.....	1.04	3.24	3.56	3.72
Normal butane.....	4.68	18.50	21.16	22.41
Iso pentane.....	.85	6.03	8.08	9.27
Normal pentane.....	1.14	9.62	13.82	16.40
Iso hexane.....	.24	2.94	5.18	7.03
Normal hexane.....	.26	3.89	7.75	11.71
Iso heptane.....	.05	1.07	2.66	5.19
Normal heptane.....	.07	1.51	4.14	9.21
Residue.....	.00	.09	.58	1.64
Total.....	10.01	50.01	70.10	89.90
Weight % Vapor.....	9.16	42.70	63.30	85.90

Figs. 8 through 15 give the comparison between the calculated and the experimental vaporization curves for all the mixtures studied. Fig. 16 gives the comparison between the vaporizations of the individual compounds as computed by Raoult's Law from the composition of the original mixture and as obtained experimentally. Fig. 16 is plotted on a mol basis and the other figures are on a weight basis.

TABLE XI
CALCULATED VAPORIZATION OF 75A

Temperature		Calculated Mol % Vaporized	Weight % Vaporized
Deg. C.	Deg. F.		
43.7	110.6	10	8.85
48.2	118.7	30	24.35
53.5	128.4	50	46.40
59.6	139.2	70	66.40
68.7	155.6	90	87.80

CALCULATED VAPORIZATION OF 48

48.3	119.0	10	8.38
53.8	129.0	30	26.40
59.7	139.2	50	45.60
65.5	150.0	70	65.20
71.9	161.5	90	86.80

CALCULATED VAPORIZATION OF 48A

47.3	117.2	10	8.56
56.0	133.0	40	36.60
73.9	166.0	80	75.00

TABLE XII

COMPOSITION OF GASOLINE-OIL MIXTURE NO. 5 (GASOLINE 89.3 MOL %). THIS
SAMPLE IS MADE UP OF THE RICH OIL FROM THE FIELD AND
GASOLINE NO. 72

Compound	Amount in Rich Oil	Amount in Sample 72	Mol % Analysis of Mixture
Propane.....	.194	2.89	3.08
Iso butane.....	.198	3.28	3.48
Normal butane.....	.527	19.80	20.33
Total butanes.....	.725	23.08	23.81
Iso pentane.....	.333	8.35	8.68
Normal pentane.....	.289	14.91	15.20
Total pentanes.....	.622	23.26	23.88
Iso hexane.....	.099	6.65	6.75
Normal hexane.....	.151	11.41	11.56
Total hexanes.....	.250	18.06	18.31
Iso heptane.....	.052	5.60	5.65
Normal heptane.....	.077	10.55	10.62
Total heptanes.....	.129	16.15	16.25
Residue.....	.111	3.70	3.81
Absorption oil.....	10.60		10.60
Total.....			100.00

Experimental runs on this sample are numbered 17, 18, 19 and 20.

TABLE XIII

CALCULATED VAPORIZATION OF MIXTURE 5 AT 740 MM.

Per cent Vaporized {	Wt.	10.20	21.50	34.20	47.20	61.50
	Mol.	15	30	45	60	75
Temperature {	Deg. C.	30.25	40.5	50.0	62.0	78.5
	Deg. F.	86.4	104.9	122.0	143.5	173.0
Propane		2.01	2.64	2.88	2.99	3.05
Iso butane		1.49	2.44	2.98	3.24	3.40
Normal butane		6.95	12.75	16.50	18.50	19.70
Total butanes		8.44	15.22	19.48	21.74	23.10
Iso pentane		1.41	3.41	5.45	7.06	8.07
Normal pentane		1.94	5.05	8.60	11.75	13.90
Total pentanes		3.36	8.46	14.05	18.81	21.97
Iso hexane		.44	1.30	2.65	4.28	5.80
Normal hexane		.50	1.53	3.56	6.40	9.41
Total hexanes		.94	2.83	6.21	10.68	15.21
Iso heptane		.11	.39	.97	2.16	3.93
Normal heptane		.15	.52	1.34	3.38	6.76
Total heptanes		.26	.91	2.31	5.54	10.69
Residue		.01	.05	.12	.38	1.20

TABLE XIV

COMPOSITION OF GASOLINE-OIL MIXTURE NO. 6 (GASOLINE 73.10 MOL. %). SAMPLE
MADE UP FROM RICH OIL AND SAMPLE 72

Compound	Mols in Rich Oil	Mols in Fuel 72	Mol per cent Analysis of Mixture
Ethane	.032		.032
Propane	.483	2.27	2.75
Iso butane	.492	2.58	3.07
Normal butane	1.31	15.60	16.91
Total butanes	1.80	18.18	19.98
Iso pentane	.826	6.57	7.40
Normal pentane	.716	11.75	12.46
Total pentanes	1.54	18.32	19.86
Iso hexane	.246	5.24	5.40
Normal hexane	.374	9.00	9.37
Total hexanes	.620	14.24	14.86
Iso heptane	.129	4.44	4.57
Normal heptane	.190	8.31	8.50
Total heptanes	.319	12.75	13.07
Residue	.30	2.92	3.22
Absorption oil	26.90		26.90
Total			100.0

Experimental Vaporizations on this oil are numbered 21, 22, and 23.

TABLE XV

CALCULATION OF VAPORIZATION OF MIXTURE NO. 6 AT 740 MM.

Per cent Vaporized { Wt. Mol.	5.25 10.	13.90 25.	21.20 35.	26.90 45.	34.20 55.
Temperature { Deg. C. Deg. F.	34 93.2	46.1 114.8	56.7 134.	69 156	83 181.5
Ethane.	.03	.03	.03	.03	.03
Propane.	1.55	2.34	2.52	2.64	2.70
Iso butane.	1.04	2.10	2.51	2.78	2.92
Normal butane.	4.52	10.32	12.90	14.72	15.80
Total butanes.	5.56	12.42	15.41	17.50	18.72
Iso pentane.	.91	2.82	4.27	5.51	6.37
Normal pentane.	1.19	3.96	6.41	8.69	10.40
Total pentanes.	2.10	6.78	10.68	14.20	16.77
Iso hexane.	.28	1.03	1.91	2.97	3.99
Normal hexane.	.30	1.26	2.56	4.30	6.17
Total hexanes.	.58	2.29	4.46	7.27	10.16
Iso heptane.	.07	.31	.69	1.07	2.31
Normal heptane.	.10	.42	1.03	2.07	3.77
Total heptanes.	.17	.73	1.72	3.14	6.08
Residue.	.01	.04	.10	.26	.57

TABLE XVI

COMPOSITION OF GASOLINE-OIL MIXTURE NO. 7 (GASOLINE 35.3 MOL. %). SAMPLE
MADE UP FROM RICH OIL AND FUEL 72

Compound	Mols in Rich Oil	Mols in Fuel 72	Mol per cent Analysis of Mixture
Ethane.	.077		.077
Propane.	1.15	.83	1.98
Iso butane.	1.18	.93	2.11
Normal butane.	3.14	5.62	8.76
Total butanes.	4.32	6.55	10.87
Iso pentane.	1.98	2.37	4.35
Normal pentane.	1.72	4.23	5.95
Total pentanes.	3.70	6.60	10.30
Iso hexane.	.59	1.88	2.47
Normal hexane.	.90	3.23	4.13
Total hexanes.	1.49	5.11	6.60
Iso heptane.	.31	1.58	1.89
Normal heptane.	.46	2.99	3.45
Total heptanes.	.77	4.57	5.34
Residue.	.17	1.04	1.21
Absorption oil.	63.65		63.65

Experimental vaporizations on this oil are numbered 24, 25 and 26

TABLE XVII
CALCULATED VAPORIZATION OF SERIES 2. AT 740 MM.

Per cent Vaporized {	Wt. Mol.	1.90	4.12	6.12	8.04
		5	10	15	20
Temperature {	Deg. C. Deg. F.	55	60.8	78.6	94
		130.5	142.0	173.5	201
Ethane		.07	.07	.07	.08
Propane		.99	1.40	1.69	1.80
Iso Butane		.62	1.05	1.48	1.72
Normal butane		2.02	3.76	3.17	6.80
Total butanes		2.64	4.81	5.56	8.52
Iso pentane		.48	1.04	1.93	2.68
Normal pentane		.53	1.16	2.30	3.38
Total pentanes		1.01	2.20	4.23	6.06
Iso hexane		.12	.28	.61	1.02
Normal hexane		.14	.33	.80	1.42
Total hexanes		.26	.61	1.41	2.42
Iso heptane		.03	.82	.21	.42
Normal heptane		.04	.12	.30	.63
Total heptanes		.07	.94	.51	1.05
Residue		.00	.01	.04	.08

TABLE XVIII
CALCULATED VAPORIZATION OF TETRALIN-GASOLINE MIXTURE. COMPOSITION 50
MOL % MIXTURE NO. 72

Temperature		Calculated Mols	Weight Per cent
Deg. C.	Deg. F.		
42.0	107.5	5	2.94
67.8	153.0	20	13.70
87.0	188.0	30	21.20

DISCUSSION OF RESULTS

When this investigation was started it was planned to determine the actual deviations from Raoult's Law for each of the compounds present in natural gasoline. The investigation was started, using mixture 72 as representative of commercial natural gasoline (Grade BB). The plan was to vaporize this mixture, and mixtures of this gasoline with absorption oils of various kinds to study their vaporization characteristics particularly in regard to the application of Raoult's Law.

Vaporizations were made on these mixtures with results as reported in runs 1 through 5, and 17 through 26. In each of these

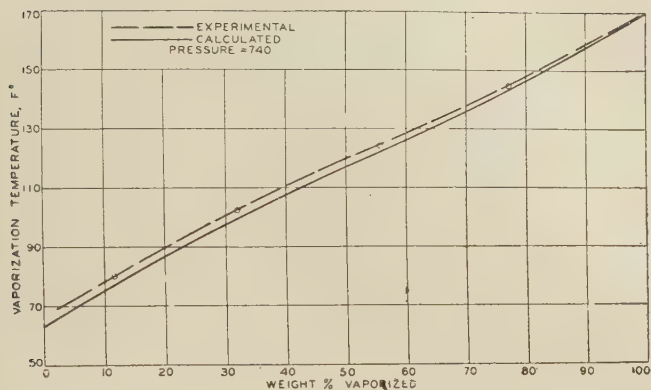


FIG. 8. Vaporization of Mixture 72.

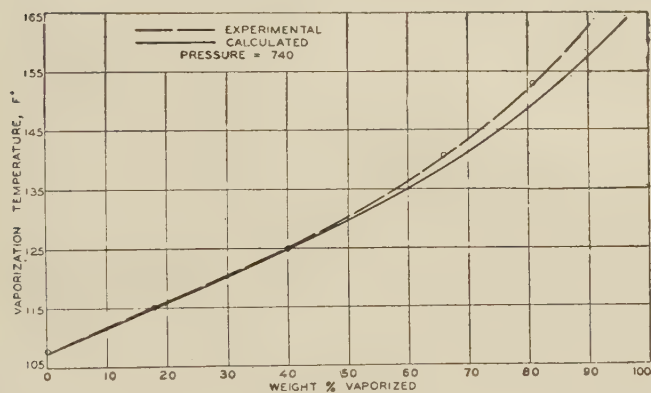


FIG. 9. Vaporization of Mixture 75A.

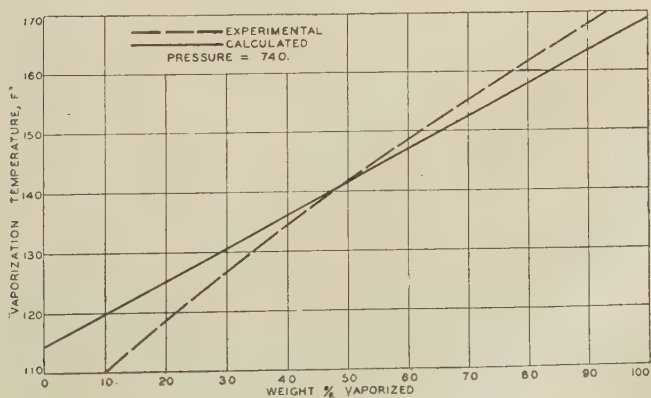


FIG. 10. Vaporization of Mixture 48.

vaporizations, analyses were made of the overhead vapors and in many cases also of the liquid residues in order that the actual amounts of each compound vaporized could be experimentally determined, and compared with the values calculated from the original composition by means of Raoult's Law.

The first observation was that the vaporization curves for the mixture 72 (Fig. 8) indicated entirely different vaporization characteristics than had been previously observed in the case of mixture 48 (Fig. 10). The peculiar deviation in the case of mixture 48 led to the belief that the compounds more volatile than pentane exerted a greater partial pressure and those less volatile a lower partial pressure than would be calculated by Raoult's Law, as had been suggested by Calingaert and Hitchcock in their studies of binary mixtures. It will also be noted in the analysis of mixture 48 that no propane is present and only a small amount of butane, the principal part of the mixture being pentane and heavier material.

If this reasoning be correct it would seem, if the mixture having butane as its most volatile component (No. 48) was more volatile at low vaporizations than would be calculated by Raoult's Law, that certainly a mixture with much larger amounts of butane and considerable propane (No. 72) ought to exhibit this same characteristic to a greater degree. However, this was not the case, as mixture 72 is slightly less volatile for all percentages vaporized than is calculated by Raoult's Law.

No satisfactory explanation could be offered for this difference, without further information. In the hope of obtaining this information, another natural gasoline intermediate in volatility (No. 75A) was vaporized and compared with the calculated vaporizations (Fig. 9). In this case still different vaporization characteristics appeared. From Fig. 9 it will be seen that the experimental curve follows the calculated vaporizations. In this case, still different vaporization characteristics appeared. From Fig. 9 it will be seen that the experimental curve follows the calculated curve for practically 50 per cent of the sample vaporized.

No adequate explanation of these data could be offered on the basis of the considerations just discussed. When the analyses of the three mixtures were compared it was observed that mixture 48 contained 43.7 per cent of pentane and butane, mixture 75A contained 50.0 per cent of pentane and butane, and mixture 72 contained 56.5

per cent of propane, butane, and pentane. It was also observed from the data on the vaporization of these mixtures, that mixture 48 was more volatile at low vaporizations than was calculated, mixture 75A checked the calculated values and mixture 72 was somewhat less volatile than would be calculated from Raoult's Law.

From empirical considerations, it seemed that the characteristics of mixture 48 might be so modified by the addition of the proper amount of pentane as to show the same deviations as mixture 75A or 72. Accordingly, mixture 48A was prepared by adding to mixture 48 sufficient pentane to give a mixture having about the same per cent of pentane as 75A. This mixture was studied in runs 15 and 16 which are compared with the calculated vaporization in Fig. 11.

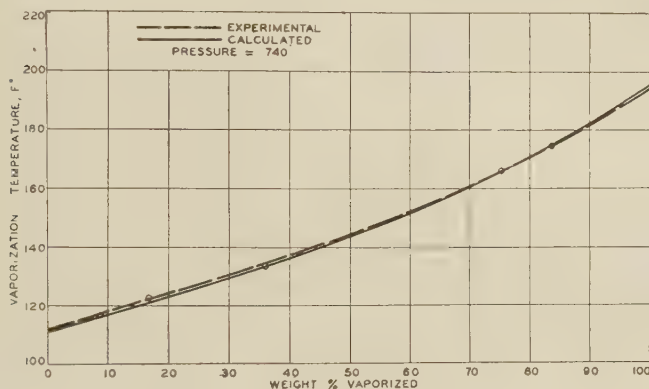


FIG. 11. Vaporization of Mixture 48A.

As was expected, the vaporization characteristics of mixture 48A corresponded to those of 75A for the lower amounts vaporized. These data show that in so far as Raoult's Law applies to complex mixtures, the properties of the mixture are entirely dependent upon its composition. For this reason the vapor pressure of natural gasolines and similar mixtures cannot be calculated with any precision or confidence by Raoult's Law.

Fig. 17 gives one set of curves showing the comparison between the actual amounts of the individual compounds vaporized and as calculated by Raoult's Law. In the case of mixture 72 each of the compounds shows approximately the same deviation (Fig. 17) as is also indicated by the total vaporization curve (Fig. 8). Considera-

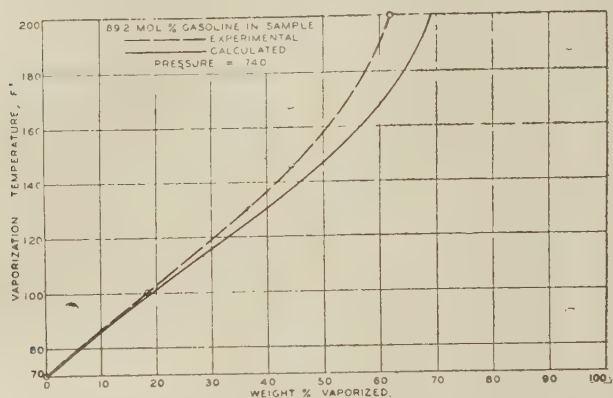


FIG. 12. Vaporization of Oil-Gasoline Mixture.

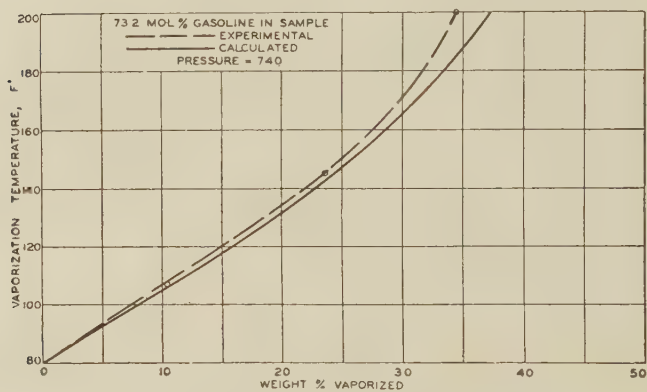


FIG. 13. Vaporization of Oil-Gasoline Mixture.

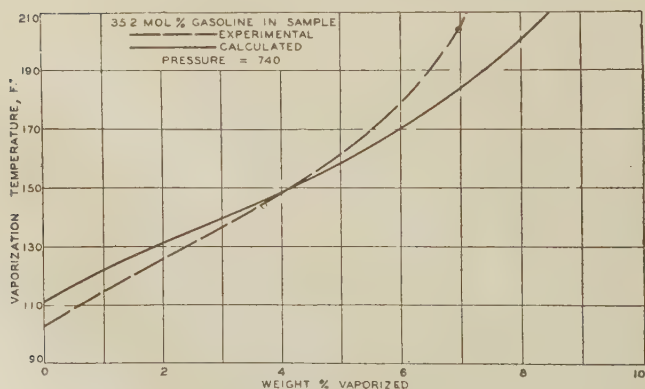


FIG. 14. Vaporization of Oil-Gasoline Mixture.

tion of these two curves, as well as other similar tests, indicates that the trend of the deviations for the individual compounds can be estimated from the overall vaporization curve.

In the study of gasoline mixed with absorption oil, No. 1, vaporizations at different temperatures and concentrations of gasoline in oil were made. The individual compounds exhibited the same vaporization characteristics when determined by actual analysis as

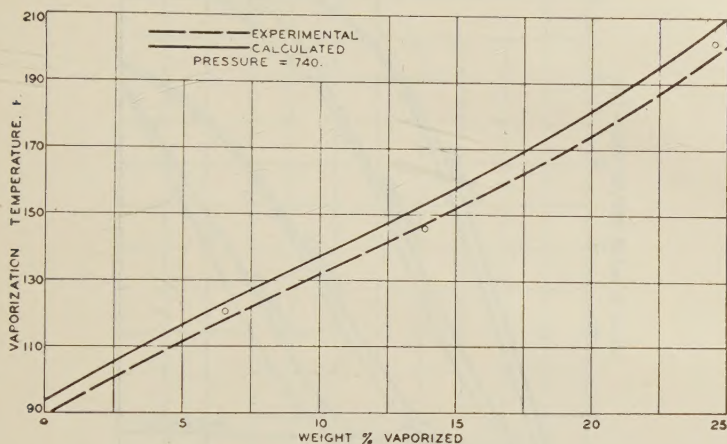


FIG. 15. Vaporization of 50-50 Tetralin-Gasoline Mixture.

are indicated by the integral vaporization curves for these mixtures (Figs. 8, 12, 13, and 14). These figures indicate for this particular mixture of gasoline and absorption oil that Raoult's Law used with good precision up to about 50 per cent of the gasoline vaporized.

Fig. 15 shows the vaporization calculated by Raoult's Law, and as obtained experimentally, of mixture 9, containing gasoline and tetralin. This figure indicates that Raoult's Law may be applied to tetralin-gasoline mixtures with about the same degree of accuracy as obtainable when applied to the ordinary run of absorption oils or naphthas. The fact that previous investigations do not show good agreement can be explained almost entirely by the fact that the composition of the original sample determines the vaporization characteristics. In most cases, the number of different samples used was insufficient to bring out this point and conclusions were drawn on results obtained from similar mixtures.

The results which Podbielniak ⁷ gives for differential vaporization could have been predicted from the results of the present investiga-

tion on the basis of mixture composition. Mixture 72 has a composition very similar to that which Podbielniak used for differential vaporizations and it shows fair agreement with Raoult's Law. The conclusions he drew from his equilibrium flash vaporization are not

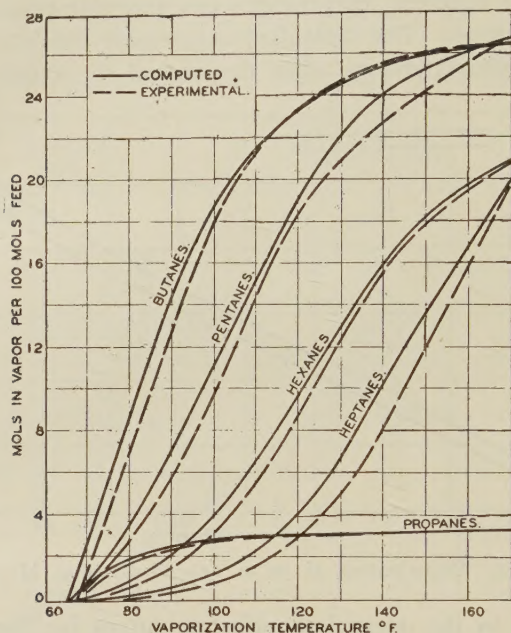


FIG. 16. Vaporization of Mixture 72.

justified inasmuch as he made only one vaporization. Although this was made on mixture 48, the per cent vaporized was such that it showed less than five per cent deviation from the vaporization calculated by Raoult's Law.

CONCLUSIONS

Deviations from Raoult's Law as applied to complex mixtures are dependent upon the relative composition of a mixture of similar substances as well as upon the similarity or dissimilarity of the components in the mixture.

For engineering calculations when an accuracy of 5 to 15 per cent is considered satisfactory, Raoult's Law may be used with fairly satisfactory results. When greater accuracy is desired, little confidence can be placed in results calculated by means of Raoult's Law.

